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Issued March 9, 1907.

U. S. DEPARTMENT OF AGRICULTURE,

BUREAU OF ANIMAL INDUSTRY.—BULLETIN NO. 94.

A. D. MELVIN, CHIEF OF BUREAU.

INVESTIGATIONS IN THE USE OF THE BOMB CALORIMETER.

IN COOPERATION WITH THE PENNSYLVANIA STATE COLLEGE AGRICULTURAL EXPERIMENT STATION.

BY

J. AUGUST FRIES, M. S.,

Assistant Expert in Animal Nutrition.

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LETTER OF TRANSMITTAL.

U. S. Department of Agriculture,
Bureau of Animal Industry,
Washington, D. C., December 15, 1906.

Sir: I have the honor to transmit herewith, and to recommend for publication as a bulletin of this Bureau, a manuscript entitled "Investigations in the Use of the Bomb Calorimeter," by J. August Fries, M. S., assistant expert in animal nutrition. The experiments described in this article are a part of the investigations in animal nutrition conducted at the Pennsylvania State Agricultural Experiment Station by cooperation between that station and this Bureau. The particular objects and value of the work reported by Mr. Fries are described in the accompanying letter by Doctor Armsby, the expert in charge of the cooperative investigations.

Respectfully,

A. D. Melvin, *Chief of Bureau.*

Hon. James Wilson,
Secretary of Agriculture.

LETTER OF SUBMITTAL.

STATE COLLEGE, PA., *October 13, 1906.*

SIR: The investigations upon the energy values of feeding stuffs which are being carried on, with the aid of the respiration calorimeter, in cooperation with the Pennsylvania Experiment Station, depend in large part for their value upon accurate determinations of the heats of combustion of the feeds and of the visible excreta. The bomb calorimeter of Berthelot in its various modifications is recognized as the most convenient and accurate instrument for this purpose which has thus far been devised, and the modification of it known as the Atwater-Hempel bomb has been used in these investigations. Since the values obtained with this instrument are fundamental to the research, it is obvious that critical study should be given to the accuracy of the method employed.

I have the honor to submit herewith the results of experiments by Mr. J. August Fries, assistant expert in animal nutrition, upon this subject. These experiments have been made during the past four years in connection with the investigations in animal nutrition reported or in progress, and their results indicate some of the possible sources of error in the method and the precautions necessary in its use to secure accuracy, while they also show the need of further experiments on the same subject. It is hoped that these results may be of value to other investigators in the same field.

Very respectfully,

HENRY PRENTISS ARMSBY,
Expert in Animal Nutrition.

Dr. A. D. MELVIN,
Chief of the Bureau of Animal Industry.

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INVESTIGATIONS IN THE USE OF THE BOMB CALORIMETER.

INTRODUCTORY.

In scientific investigations, as well as in technical work, it is often of very great importance to know the exact heat of combustion, or, in other words, the energy value of a substance. To determine the heats of combustion of organic compounds it is necessary to completely oxidize them to their most simple or stable decomposition products and measure the heat evolved. Several methods have been used for such determinations, but the latest and best for the greater number of compounds is undoubtedly the Berthelot or bomb-calorimeter method, where the substance to be analyzed is burned in oxygen gas under high pressure. Detailed descriptions of this apparatus and directions for its use are found in various scientific works, hence no full description need be given here.

THE APPARATUS USED.

The apparatus used for the work described in this paper was the Atwater-Hempel bomb calorimeter, which is a modification of the Berthelot apparatus.[a] The main features only of its construction and manipulation will be referred to briefly at this time.

The apparatus consists of the bomb proper, which is a strong steel cup lined on the inside with platinum, and of a platinum-lined top which rests on a lead washer and is firmly held in place by a threaded collar. A cylindrical vessel of Britannia metal is used for holding the water in which the bomb is immersed. The apparatus is provided with a stirring arrangement operated by means of an electric motor. Outside of this metal vessel are two concentric protecting cylinders made of indurated fiber, each provided with a cover. These fiber cylinders, with the dead air spaces between them, serve to insulate and protect the metal vessel and the water as far as possible from being affected by any change of outside or room temperature or circulation of air. A Beckmann mercury thermometer, which can be read to 0.001° C. with accuracy, is used for taking the temperature of the water.

MANIPULATION OF THE APPARATUS.

The substance to be burned, if solid, is pressed into a tablet of convenient size, placed in a platinum capsule, which is supported on a

[a] U. S. Dept. Agr., Office of Experiment Stations Bul. 21. Conn. (Storrs) Sta. Rept., 1897, p. 199.

platinum wire attached to the top or cover of the bomb, and adjusted so that the substance will come in contact with the fine iron fuse wire by means of which it is ignited. The bomb is then charged with oxygen gas to a pressure of at least 20 atmospheres. It is immersed in the weighed quantity of water, the electric connections are made, and the covers adjusted and clamped so that the stirrer will not rub. After placing the thermometer in position the stirrer is started and the temperature of the water taken. It is intended to have the water as much colder than the surrounding air before the combustion as it will be warmer after the combustion. As soon as a uniform rate of change in the water temperature has been established the substance is ignited. For this purpose an electric current strong enough to fuse instantly the fine iron wire is allowed to pass through, and by the burning of the fuse wire the substance in the capsule is also instantly ignited. The combustion is only of a few seconds' duration, and the heat formed is quickly transmitted through the bomb to the surrounding water. Readings of the thermometer are taken every minute, and from the rise in temperature of the water the heat generated is calculated.

CALCULATION OF RESULTS.

In the calculation of the results it is necessary to apply several corrections. Not only the fixed weighed quantity of water but the whole system—bomb, stirrer, metal vessel, etc.—is heated up to the same degree, therefore the correct thermoequivalent of it must be determined and used. Thermometer readings must be corrected according to the individual thermometer used. Corrections are also made for the influence of the surrounding air temperature, the heat generated by the burning of the fuse wire, the formation of nitric acid in the bomb, and the lag of the thermometer.

The formula which has been used in working out the correction for the outside air influences is the Regnault-Pfaundler formula, given in Wiley's Principles and Practice of Agricultural Analysis, Volume III, page 572, and the following example will serve to illustrate the main points to be observed in connection with the determination and calculation of the heat of combustion.

Formula:

$$\frac{v-v^1}{t^1-t}\left(\sum_{1}^{n-1}\theta_r+\frac{\theta_n+\theta_1}{2}-n\theta\right)-(n-1)v=\Sigma\Delta t.$$

$\sum_{1}^{n-1}\theta_r$=sum of θ readings minus 1 increased by an arbitrary factor $\frac{\theta_2-\theta_1}{9}$

v = average rate of radiation during preliminary period.
v^1 = average rate of radiation during end period.
θ = number of readings during combustion period.
t = average of preliminary thermometer readings.
t^1 = average of end period thermometer readings.

Example: Cellulose.
Cellulose, dried at 105° C. 1.0035 gram.
Iron fuse wire 0.0118 − 0.0018 = 0.0100 gram = 16 calories.
Oxygen pressure = 24 atmospheres.
Room temperature, 21° C.
Water temperature, 19° C. at beginning.
HNO_3 titrated = 13.5 c. c. NaOH sol. = 13.5 calories.
Cellulose ignited instantly.

Thermometer readings begin,	1.220,	1.220,	1.220,	1.221,	1.221,	1.221.
Corrected readings begin,	1.2265,	1.2265,	1.2265,	1.2275,	1.2275,	1.2275.

Combustion period,	1.221,	2.630,	2.933,	2.952,	2.952.
Corrected readings,	1.2275,	2.6414,	2.9450,	2.9640,	2.9640.

End period,	2.952,	2.949,	2.945,	2.941,	2.937.
Corrected reading,	2.9640,	2.9610,	2.9570,	2.9530,	2.9490.

$$v = 0.0002.$$
$$t = 1.2270.$$
$$\theta = 5.$$
$$v^1 = -0.0038.$$
$$t^1 = 2.9565.$$

$$\frac{0.0002 - (-0.0038)}{2.9565 - 1.2270}\Big(9.9350 + 2.0958 - 6.1350\Big) - 0.0008 = +0.013°.$$

$$\Sigma\, \Delta\, t = +0.013°.$$

Last reading of combustion period,	+ 2.9640° C.
First reading of combustion period,	− 1.2275° C.
Correction for outside air,	+ 0.0130° C.
Correction for thermometer lag,	− 0.0006° C.
	1.7489° C.
Correction for excess oxygen,	+ 0.0003° C.
Correction for impurities in oxygen, −	0.0151° C.
Corrected rise in temperature,	+ 1.7341° C.

Water value of bomb system with 20 atmospheres (2,439.2) × rise =	4229.82 calories.
Correction for fuse wire,	− 16.00 calories.
Correction for HNO_3,	− 13.50 calories.
	4229.32 calories.

4229.32 ÷ 1.0035 = 4185.7 calories per gram of cellulose.

Should for some reason the current of electricity remain on for a few seconds before the wire fuses, correction should be made for the heat generated by the current.

IMPORTANCE OF THE APPARATUS IN CALORIMETRIC DETERMINATIONS.

Not only in physical and chemical laboratories do calorimetric determinations find application, but they have acquired special prominence in connection with physiological investigations and research work, and it is in this line of work that at the present time their application in the agricultural science has been found to be of so great importance. Thus, the very elaborate, time-consuming, and expensive nutrition investigation experiments with cattle by the use of the respiration calorimeter are so planned that the successful solving of the question of energy metabolism in the animal body rests almost entirely upon the bomb calorimeter—upon its efficiency in quickly and accurately determining the heats of combustion of feed and excreta. Being, then, a most important part of the whole plan, and since so much depends upon the work of this apparatus, one is not justified, because much work has been done with it in the past, in assuming that it is perfect in all respects, or that it is adapted alike to all kinds of organic substances. Instead, it should be severely tested from different points of view, and that was the object of this work.

EARLIER DETERMINATIONS OF HEATS OF COMBUSTION.

To begin with, it may be well to look a little into the work already done, and note the condition in which our knowledge of the heat values of organic substances is at the present time, and how well different investigators agree in their determinations. For this purpose, as well as to get a general idea of heat values, I have, without going back to the original source of the information, collected and tabulated a large number of results upon the heats of combustion of the more common organic substances as obtained by various investigators. The values are taken from text-books and scientific reference books, some of which are still in use in schools and elsewhere.

To make the tables as condensed as possible the works or books referred to are represented in one column, each book by a single number, and the investigators in another column by the first letters of their respective names.

TABLE I.—*Heats of combustion of 1-gram substance, expressed in small calories.*

Substance.	Formula.	Calories.	References.[a]	Investigators.[a]
ELEMENTS, ETC.				
Hydrogen	H_2	34,462.0	1,3	F. & S.
Hydrogen (8 investigators)	H_2	[b]34,154.3	10	F. & S.
Do	H_2	[c]34,800.0	10	H.
Carbon	C	7,770.1	10	F. & S.
Charcoal (wood)	C	8,080.0	1,3,10	F. & S.
Charcoal (sugar)	C	7,714.0	10	Gr.
Do	C	8,039.8	10	F. & S.
Do	C	7,965.0	10	Sch.
Diamond (to CO_2)	C	7,859.0	10	B. & P.
Diamond (to CO)	C	2,141.7	10	B.
Iron (to Fe_2O_3)	Fe	1,600.0	9	
Iron (to FeO)	Fe	1,352.6	10	F. & S.
Sulphur	S_2	2,260.3	10	F. & S.
Do	S_2	2,165.6	10	B.
Sulphur (soft)	S_2	2,220.5	10	F. & S.
Do	S_2	2,162.5	3	F. & S.
CO to CO_2		2,436.0	3	F. & S.
Do		2,431.0	10	An.
Do		2,402.7	10	F. & S.
Do		2,438.6	10	B.
Do		2,441.7	10	Th.
Nitrogen to HNO_3 (sol.)	N_2	1,022.6	8	
NO to NO_2		652.3	10	Th.
PROTEIDS, ETC. (ALBUMINOIDS.)				
Gluten		5,990.3	2	B.
Do		6,141.0	2	D.
Elastin		5,961.3	1,2,10	St. & L.
Plant fibrin		5,832.3	2,10	B. & A.
Do		5,941.6	2,10	St. & L.
Do		6,231.0	1,2	D.
Serum albumin		5,917.8	1,2,8,10	St. & L.
Syntonin		5,907.8	2,1	St. & L.
Hemoglobin		5,910.0	2,10	B. & A.
Do		5,914.8	1,3	B. & A.
Do		5,885.1	1,2,3,10	St. & L.
Do		5,950.0	2	Ru.
Do		5,949.0	1,2,3,10	D.
Milk casein		5,626.4	2,10	B. & A.
Do		5,867.0	2,3,8,10	St. & L.
Do		5,629.2	1,3	B. & A.
Do		5,717.0	1,2,3,10	St.
Do		5,785.0	2	D.
Do		5,849.6	2,3,10	St. & L.
Do		5,858.0	1	St. & L.
Do		5,855.6	1	D.
Yolk of egg		8,112.4	2,3	B. & A.
Yolk of egg (fat free)		5,840.9	3,10	St. & L.
Legumin		5,793.1	1,2,10	St. & L.
Do		5,573.0	2	D.
Vitellin		5,780.6	2,10	B. & A.
Do		5,745.1	1,2,3,10	St. & L.
Do		5,784.1	3	St. & L.

[a] Abbreviations:

Works referred to—

1. Bunge, Physiological Chemistry, fourth German edition, 1902.
2. Armsby, Principles of Animal Nutrition, 1904, and U. S. Department of Agriculture, Office of Experiment Stations, Bulletin 21.
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4. Tollen, Handbuch I der Kohlehydrate, 1898.
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7. Jones, Elements of Physical Chemistry, 1903.
8. Wiley, Principles and Practice of Agricultural Analysis, Vol. III, 1897.
9. Journal American Chemical Society, Vol. XXV, 1903.
10. Landolt & Börnstein, Physikalisch-Chemische Tabellen, 1894.

Investigators—

A. André.
An. Andrews.
B. Berthelot.
Bu. Bunson.
D. Danilewsky.
Du. Dulong.
F. Favre.
Fo. Fogh.
Fr. Frankland.
Gi. Gibson.
Go. Gottlieb.
Gr. Grassi.
H. Hess.
He. Herzberg.
J. Jahn.
K. Kleber.
L. Langbein.
Lu. Luginni.
M. Matignon.
O. Ogier.
P. Petit.
Rch. Rechenberg.
Re. Recoura.
Ro. Rodolz.
Ru. Rubner.
S. Silbermann.
Sch. Schwackhöfer.
St. Stohmann.
T. Tower.
Th. Thomsen.
V. Vieille.

[b] Lowest.

[c] Highest.

TABLE I.—*Heats of combustion of 1-gram substance, expressed in small calories*—Cont'd.

Substance.	Formula.	Calories.	References.	Investigators.
PROTEIDS, ETC. (ALBUMINOIDS)—CON.				
Egg albumin		5,687.4	1,2,10	B. & A.
Do		5,735.2	1,2,3,8,10	St. & L.
Do		5,579.0	1,2,3,10	St.
Do		5,690.6	3	St.
Muscle (fat free and water)		5,728.4	2,10	B. & A.
Muscle (extracted)		5,720.5	2,8,10	St. & L.
Muscle (fat free)		5,662.6	2,10	St. & L.
Do		5,324.0	2,10	St.
Muscle (fat free, ash free)		5,656.0	2,10	Ru.
Do		5,640.9	2,10	St. & L.
Do		5,345.0	10	Ru.
Albumin cryst		5,672.0	1,2,10	St. & L.
Do		5,598.0	1,2,10	St.
Blood fibrin		5,529.1	2,10	B. & A.
Do		5,637.1	2,3,10	St. & L.
Do		5,511.0	1,2,3,10	St.
Do		5,709.0	2	D.
Do		5,772.0	1	D.
Do		5,532.4	3	St.
Do		5,567.3	3	St.
Albumin (Harnack's)		5,553.0	2	St. & L.
Wool		5,564.2	2	B. & A.
Do		5,510.2	2	St. & L.
Congluten		5,479.0	2,10	St. & L.
Do		5,362.0	2,10	St.
Fibrin of skin		5,355.1	2,10	St. & L.
Peptone		5,298.8	1,2,3,8,10	St. & L.
Do		5,069.0	2	D.
Do		4,876.0	1	D.
Do		4,914.0	1	D.
Fish glue		5,240.1	2,10	B. & A.
Do		5,493.0	1,2	D.
Chondrin		5,342.4	1,2,3,10	B. & A.
Do		5,130.6	1,2,3,10	St. & L.
Do		4,909.0	2	D.
Ossein		5,410.4	1,2,10	B. & A.
Do		5,039.9	1,2,10	St. & L.
Fibroin		5,095.7	2,10	St. & L.
Do		4,979.6	2,10	St. & L.
Chitin		4,655.0	2,10	St. & L.
Do		4,650.3	2,10	B. & A.
Tunicin		4,146.8	2,10	B. & A.
Paraglobulin		5,637.0	1,2,10	St.
Legumin		5,793.0	1,10	St. & L.
Proteids (mean)		5,730.8	8	
AMIDES, ETC.				
Urea	CON_2H_4	2,530.1	2,10	B. & P.
Do	CON_2H_4	2,541.9	1,2,10	St. & L.
Do	CON_2H_4	2,465.0	1,2,5,10	St.
Do	CON_2H_4	2,537.0	1,2	D.
Do	CON_2H_4	2,523.0	2,10	R.
Do	CON_2H_4	2,121.0	1	F.
Glycocoll	$C_2H_5NO_2$	3,133.6	2,9,10	B. & A.
Do	$C_2H_5NO_2$	3,129.1	2,9,10	St. & L.
Do	$C_2H_5NO_2$	3,050.0	1	St.
Do	$C_2H_5NO_2$	3,053.0	2,10	St.
Alanin	$C_3H_7NO_2$	4,370.7	2,10	B. & A.
Do	$C_3H_7NO_2$	4,355.5	2,10	St. & L.
Leucin	$C_6H_{13}NO_2$	6,536.5	1,2,10	B. & A.
Do	$C_6H_{13}NO_2$	6,525.1	1,2,10	St. & L.
Sarkosin	$C_3H_7NO_2$	4,505.9	1,2,10	St. & L.
Hippuric acid	$C_9H_9NO_3$	5,659.3	1,2,9,10	B. & A.
Do	$C_9H_9NO_3$	5,668.2	1,2,9,10	St. & L.
Do	$C_9H_9NO_3$	5,642.0	2,5,10	St.
Aspartic acid	$C_4H_7NO_4$	2,911.1	2,10	B. & A.
Do	$C_4H_7NO_4$	3,423.0	1	St.
Do	$C_4H_7NO_4$	2,899.0	2,10	St. & L.
Tyrosin	$C_9H_{11}NO_3$	5,915.9	1,2,10	B. & A.
Asparagin	$C_4H_8N_2O_3$	3,396.8	2,10	B. & A.
Do	$C_4H_8N_2O_3$	3,514.0	2,10	St. & L.
Do	$C_4H_8N_2O_3$	3,428.0	2,10	St.
Creatin cryst	$C_4H_9N_3O_2H_2O$	3,714.1	1,2,10	St. & L.
Creatin, anhydrous	$C_4H_9N_3O_2$	4,275.4	1,2,10	St. & L.
Do		(3,206.0)	2	D.
Uric acid	$C_5H_4N_4O_3$	2,754.0	2,10	B. & M.
Do	$C_5H_4N_4O_3$	2,749.9	1,2,10	St. & L.
Do	$C_5H_4N_4O_3$	2,621.0	1,2,5,10	St.
Do	$C_5H_4N_4O_3$	2,645.0	1	Fr.

TABLE I.—*Heats of combustion of 1-gram substance, expressed in small calories*—Cont'd.

Substance.	Formula.	Calories.	References.	Investigators.
AMIDES, ETC.—continued.				
Guanin	$C_5H_5N_5O$	3,891.7	1,2	St. & L.
Guanidin	CH_5N_3	4,197.0	10	M.
Caffein	$C_8H_{10}N_4O_2$	5,231.4	1,2,10	St. & L.
FATS (ANIMAL).				
Fat of swine		9,476.9	2	St. & L.
Do		9,380.0	2,3	St.
Do		9,686.0	2	D.
Do		9,423.0	1,2	R.
Do		9,515.0	2	Gi.
Fats of oxen		9,485.7	2	St. & L.
Do		9,357.0	2,3	St.
Do		9,427.0	2	Gi.
Do		9,686.0	1	D.
Fats of sheep		9,493.6	2	St. & L.
Do		9,406.0	2,3	St.
Do		9,530.0	2	Gi.
Fat of horse		9,410.0	2	St.
Fat of dog		9,330.0	2	St.
Fat of goose		9,345.0	2	St.
Fat of duck		9,324.0	2	St.
Fat of man		9,398.0	2	St.
Sperm oil		10,001.0	2	Gi.
Butter fat		9,215.8	2	St. & L.
Do		9,192.0	2,3,10	St.
Do		9,185.0	2	Gi.
Do		9,231.3	8	
Do		9,179.0	1	St.
Do		9,230.0	10	St. & L.
Fat, mean (man, oxen, sheep)		9,365.0	10	St.
Fat, mean (dog, swine)		9,423.0	10	R.
Fat, mean (goose, duck)		9,500.0	10	St. & L.
Do		9,372.0	1	St.
FATS (VEGETABLE).				
Olive oil (expressed)		9,328.0	2,10	St.
Do		9,471.0	2	Gi.
Do		9,323.0	3	St.
Do		9,467.0	8	
Do		9,455.0	1	St.
Do		9,471.0	2	St.
Do		9,442.0	10	St.
Poppy-seed oil		9,489.0	2,10	St.
Rape-seed oil		9,489.0	2,10	St.
Do		9,619.0	2,10	St.
Do		9,621.9	10	M.
Ether extract—Various seeds		9,130.0 9,467.0	2	St.
CARBOHYDRATES, ETC.				
Arabinose	$C_5H_{10}O_5$	3,714.0	2,6,10	B. & M.
Do	$C_5H_{10}O_5$	3,722.0	8,2,6,10	St. & L.
Do	$C_5H_{10}O_5$	3,695.0	5,2,10,4	St.
Xylose	$C_5H_{10}O_5$	3,739.9	2,6,10	B. & M.
Do	$C_5H_{10}O_5$	3,746.0	2,8,6,10	St. & L.
Fucose	$C_6H_{12}O_5$	4,340.9	2,6,10	St. & L.
Rhamnose (water free)	$C_6H_{12}O_5$	4,379.3	2,6,10	St. & L.
Rhamnose (crystallized)	$C_6H_{12}O_5H_2O$	3,909.2	2,6,10	St. & L.
Sorbinose	$C_6H_{12}O_6$	3,714.5	2,6,10	St. & L.
Galactose	$C_6H_{12}O_6$	3,721.5	2,6,10	St. & L.
Do	$C_6H_{12}O_6$	3,659.0	2,4	St.
Dextrose (glucose)	$C_6H_{12}O_6$	3,762.0	2,4	B. & V.
Do	$C_6H_{12}O_6$	3,742.6	2,8,6,10	St. & L.
Do	$C_6H_{12}O_6$	3,692.0	2,4,5,10,1	St.
Do	$C_6H_{12}O_6$	3,754.0	2,10	Gi.
Do	$C_6H_{12}O_6$	3,939.0	1	Rch.
Do	$C_6H_{12}O_6$	3,760.0	6	B.
Dextrose (hydrated)	$C_6H_{12}O_6H_2O$	3,567.0	1	Rch.
Levulose (fructose)	$C_6H_{12}O_6$	3,755.0	2,8,6,10	St. & L.
Glucoheptose	$C_7H_{14}O_7$	3,732.8	2,10	B. & F.
Cane sugar (sucrose)	$C_{12}H_{22}O_{11}$	3,961.7	2,4,10,9	B. & V.
Do	$C_{12}H_{22}O_{11}$	3,955.2	8,2,6,9,10	St. & L.
Do	$C_{12}H_{22}O_{11}$	3,866.0	2,5,10	St.
Do	$C_{12}H_{22}O_{11}$	4,001.0	2,10	Ru.
Do	$C_{12}H_{22}O_{11}$	3,921.0	2,10	Gi.
Do	$C_{12}H_{22}O_{11}$	3,958.7	9	T.
Do	$C_{12}H_{22}O_{11}$	4,176.0	1	D.

TABLE I.—*Heats of combustion of 1-gram substance, expressed in small calories*—Cont'd.

Substance.	Formula.	Calories.	References.	Investigators.
CARBOHYDRATES, ETC.—continued.				
Cane sugar (sucrose)	$C_{12}H_{22}O_{11}$	4,173.0	1	Rch.
Do	$C_{12}H_{22}O_{11}$	3,959.0	1	St.
Do	$C_{12}H_{22}O_{11}$	3,908.0	4	St.
Milk sugar (lactose)	$C_{12}H_{22}O_{11}$	3,951.5	2,6,10	St. & L.
Do	$C_{12}H_{22}O_{11}$	3,877.0	1,2,4,5,10	St.
Do	$C_{12}H_{22}O_{11}$	4,162.0	1	Rch.
Do	$C_{12}H_{22}O_{11}$	3,920.0	10	Gi.
Milk sugar hydrated	$C_{12}H_{22}O_{11}H_2O$	3,777.1	2,10	B. & V.
Do	$C_{12}H_{22}O_{11}H_2O$	3,736.8	2,8,6,10	St. & L.
Do	$C_{12}H_{22}O_{11}H_2O$	3,663.0	2,4,10	St.
Do	$C_{12}H_{22}O_{11}H_2O$	3,710.0	2	Gi.
Do	$C_{12}H_{22}O_{11}H_2O$	3,945.0	1	Rch.
Do	$C_{12}H_{22}O_{11}H_2O$	3,667.0	1	St.
Do	$C_{12}H_{22}O_{11}H_2O$	3,772.2	4	B.
Do	$C_{12}H_{22}O_{11}H_2O$	3,721.8	6	Gi.
Do	$C_{12}H_{22}O_{11}H_2O$	3,724.0	10	Gi.
Maltose	$C_{12}H_{22}O_{11}$	3,949.3	2,8,6,10	St. & L.
Do	$C_{12}H_{22}O_{11}$	4,163.0	1	Rch.
Maltose hydrated	$C_{12}H_{22}O_{11}H_2O$	3,721.8	2,6,10	St. & L.
Do	$C_{12}H_{22}O_{11}H_2O$	3,932.0	1	Rch.
Trehalose	$C_{12}H_{22}O_{11}$	3,947.0	2,10,6	St. & L.
Trehalose hydrated	$C_{12}H_{22}O_{11}H_2O$	3,550.3	2,10,6	St. & L.
Raffinose (melitriose)	$C_{18}H_{32}O_{16}$	3,928.0	10	St.
Do	$C_{18}H_{32}O_{16}$	4,020.0	2,6,10	B. & M.
Do	$C_{18}H_{32}O_{16}$	4,020.8	2,6,10	St. & L.
Raffinose (melitriose) hydrated	$C_{18}H_{32}O_{16}^{6}(H_2O)$	3,400.2	2,6	St.
Do	$C_{18}H_{32}O_{16}^{6}(H_2O)$	3,399.1	10	St. & L.
Melitose	$C_{12}H_{22}O_{11}$	3,880.0	4	St.
Do	$C_{16}H_{32}O_{16}$	4,122.2	5	St.
Melezitose	$C_{18}H_{34}O_{17}$	3,913.7	2,6,10	St. & L.
Glycogen	$(C_6H_{10}O_5)n$	4,190.6	2,6	St. & L.
Cellulose	$(C_6H_{10}O_5)n$	4,200.0	2,4	B. & V.
Do	$(C_6H_{10}O_5)n$	4,185.4	2,6,10	St. & L.
Do	$(C_6H_{10}O_5)n$	4,146.0	1,2,4,10	St.
Do	$(C_6H_{10}O_5)n$	4,152.9	6	Go.
Do	$(C_6H_{10}O_5)n$	4,155.0	10	Go.
Do	$(C_6H_{10}O_5)n$	4,205.0	10	B. & V.
Dextrin (dextran)	$(C_6H_{10}O_5)n$	4,180.4	2,10	B. & V.
Do	$(C_6H_{10}O_5)n$	4,112.3	2,10,6	St. & L.
Starch	$(C_6H_{10}O_5)n$	4,228.0	2,4,10	B. & V.
Do	$(C_6H_{10}O_5)n$	4,182.5	2,6,10	St. & L.
Do	$(C_6H_{10}O_5)n$	4,123.0	2,4,10	St.
Do	$(C_6H_{10}O_5)n$	4,164.0	2,6,10	Gi.
Do	$(C_6H_{10}O_5)n$	4,479.0	1	Rch.
Do	$(C_6H_{10}O_5)n$	4,116.0	1	St.
Inulin	$(C_6H_{10}O_5)n$	4,187.1	2,10	B. & V.
Do	$(C_6H_{10}O_5)n$	4,133.5	2	St. & L.
Do	$(C_6H_{10}O_5)n$	4,070.0	2,4,10	St.
Do	$C_{36}H_{60}O_{31}$	4,133.5	6,10	St.
ALCOHOLS.				
Methyl alcohol (liquid)	CH_4O	5,260.7	5	
Do	CH_4O	5,307.1	10	F. & S.
Do	CH_4O	5,321.5	10	St. & L.
Methyl alcohol (gas)	CH_4O	5,693.7	10,5	Th.
Ethyl alcohol (liquid)	C_2H_6O	7,068.0	2,10	B. & M.
Do	C_2H_6O	7,183.6	3,10,1	F. & S.
Do	C_2H_6O	6,980.0	1	B.
Do	C_2H_6O	7,095.0	9	A.
Do	C_2H_6O	7,044.0	5	St.
Ethyl alcohol (gas)	C_2H_6O	7,402.2	10	Th.
Do	C_2H_6O	7,321.7	10	B. & M.
Do	C_2H_6O	7,394.1	5,7	
Propyl alcohol (liquid)	C_3H_8O	8,010.3	5	St.
Do	C_3H_8O	8,005.2	10	Lu.
Propyl alcohol (gas)	C_3H_8O	8,310.0	10	Th.
Do	C_3H_8O	7,301.7	5,7	
Amyl alcohol	$C_5H_{12}O$	8,958.6	10	F. & S.
Do	$C_5H_{12}O$	9,021.8	10	Lu.
Do	$C_5H_{12}O$	9,005.7	5	St.
Glycerin	$C_3H_8O_3$	(4,112.4)	2	St. & L.
Do	$C_3H_8O_3$	4,312.4	10	St. & L.
Do	$C_3H_8O_3$	4,317.0	2,10	St.
Do	$C_3H_8O_3$	4,305.0	1	St.
Do	$C_3H_8O_3$	4,265.2	10	Lu.
Erythrit	$C_4H_{10}O_4$	4,075.0	10	St.
Do	$C_4H_{10}O_4$	4,112.5	10	Lu.
Do	$C_4H_{10}O_4$	4,117.6	10	B. & M.
Do	$C_4H_{10}O_4$	4,131.3	10	St.&L.&K.
Do	$C_4H_{10}O_4$	4,132.3	10,6	St. & L.

TABLE I.—*Heats of combustion of 1-gram substance, expressed in small calories*—Cont'd.

Substance.	Formula.	Calories.	References.	Investigators.
ALCOHOLS—continued.				
Erythrit	$C_4H_{10}O_4$	4,072.7	5	St.
Mannite	$C_6H_{14}O_6$	4,001.2	2,4,10	B. & V.
Do	$C_6H_{14}O_6$	3,997.8	2,6,10	St. & L.
Do	$C_6H_{14}O_6$	3,908.0	2	St.
Do	$C_6H_{14}O_6$	3,959.0	2,6,10	Gi.
Do	$C_6H_{14}O_6$	3,939.0	10	St.
Do	$C_6H_{14}O_6$	3,936.6	5,10	St.
Arabit	$C_5H_{12}O_5$	4,024.6	6,10	St. & L.
Dulcit	$C_6H_{14}O_6$	3,975.9	6,10	St. & L.
Do	$C_6H_{14}O_6$	4,006.0	4,10	B. & V.
Do	$C_6H_{14}O_6$	3,905.9	5	St.
Quercite	$C_6H_{12}O_5$	4,293.6	6	St.
Do	$C_6H_{12}O_5$	4,329.0	6	B.
Inosite	$C_6H_{12}O_6$	3,679.6	6	St.
Do	$C_6H_{12}O_6$	3,695.1	6	B.
ACIDS.				
Formic acid (liquid)	CH_2O_2	1,271.2	5	St.
Do	CH_2O_2	1,366.8	10	J.
Do	CH_2O_2	1,347.8	10	B.
Formic acid (gas)	CH_2O_2	1,508.5	10	Th.
Acetic acid	$C_2H_4O_2$	3,490.4	2	B. & M.
Do	$C_2H_4O_2$	3,505.2	1,10	F. & S.
Do	$C_2H_4O_2$	3,498.3	7	
Do	$C_2H_4O_2$	3,553.2	5	St.
Do	$C_2H_4O_2$	3,480.0	10	J.
Do	$C_2H_4O_2$	3,555.0	10	St. & R.
Acetic acid (gas)	$C_2H_4O_2$	3,755.0	10	Th.
Propionic acid	$C_3H_6O_2$	4,968.2	5	St.
Butyric acid	$C_4H_8O_2$	5,936.9	5	St.
Do	$C_4H_8O_2$	5,647.0	1,10	F. & S.
Do	$C_4H_8O_2$	5,939.8	10	St. & Ro.
Oxybutyric acid	$C_4H_8O_3$	4,536.0	10	Lu.
Palmetic acid	$C_{16}H_{32}O_2$	9,352.9	2,10	St. & L.
Do	$C_{16}H_{32}O_2$	9,226.0	2,10	St.
Do	$C_{16}H_{32}O_2$	9,216.8	5	St.
Do	$C_{16}H_{32}O_2$	9,264.8	10	Lu.
Do	$C_{16}H_{32}O_2$	9,316.5	10	F. & S.
Stearic acid	$C_{18}H_{36}O_2$	9,429.0	2,10	St.
Do	$C_{18}H_{36}O_2$	9,716.5	1,10	F. & S.
Do	$C_{18}H_{36}O_2$	9,412.0	1	St.
Do	$C_{18}H_{36}O_2$	9,886.0	1	Rch.
Do	$C_{18}H_{36}O_2$	9,745.0	1	R.
Oleic acid	$C_{18}H_{34}O_2$	9,494.9	10	St. & L.
Malonic acid	$C_3H_4O_4$	1,998.2	2,10	B. & Lu.
Do	$C_3H_4O_4$	1,960.0	2	St.
Do	$C_3H_4O_4$	1,998.3	10	St. & L.
Succinic acid	$C_4H_6O_4$	3,006.2	2,10	B. & Lu.
Do	$C_4H_6O_4$	3,019.0	2	St.
Do	$C_4H_6O_4$	2,996.0	1	Rch.
Do	$C_4H_6O_4$	2,937.0	1	St.
Do	$C_4H_6O_4$	3,026.3	10	St. & L.
Tartaric acid	$C_4H_6O_6$	1,745.0	1,2	St.
Do	$C_4H_6O_6$	1,407.0	1	Rch.
Citric acid	$C_6H_8O_7$	2,477.9	2,10	B. & Lu.
Do	$C_6H_8O_7$	2,397.0	2,10	St.
Do	$C_6H_8O_7$	2,477.9	2,10	B. & Lu.
Citric acid, hydrated	$C_6H_8O_7H_2O$	2,250.4	10	Lu.
Oxalic acid	$C_2H_2O_4$	659.0	1	Rch.
Do	$C_2H_2O_4$	569.0	1	St.
Do	$C_2H_2O_4$	571.0	10	St.
Do	$C_2H_2O_4$	678.6	10	St. & L.
Do	$C_2H_2O_4$	672.5	10	J.
Benzoic acid	$C_7H_6O_2$	6,360.5	5	St.
Do	$C_7H_6O_2$	6,322.3	9	St. & L.
Do	$C_7H_6O_2$	6,322.1	9	B. & Lu.
Do	$C_7H_6O_2$	6,281.0	10	St.
Do	$C_7H_6O_2$	6,315.0	10	St. & Ro.
Do	$C_7H_6O_2$	6,345.0	10	B. & Rc.
Do	$C_7H_6O_2$	(7,663.0)	5	St.
Salicylic acid	$C_7H_6O_3$	7,236.0	5	St.
Do	$C_7H_6O_3$	5,286.2	10	St. & L.
Do	$C_7H_6O_3$	5,326.0	10	B. & Rc.
HYDROCARBONS, ETC.				
Methane	CH_4	13,063.0	3,10	F. & S.
Do	CH_4	13,218.9	5,7	Th.
Do	CH_4	13,243.7	10	Th.
Do	CH_4	13,275.0	10	B.

TABLE I.—*Heats of combustion of 1-gram substance, expressed in small calories*—Cont'd.

Substance.	Formula.	Calories.	References.	Investigators.
HYDROCARBONS, ETC.—continued.				
Ethane	C_2H_6	12,144.2	7,5	
Do	C_2H_6	12,346.7	10	Th.
Do	C_2H_6	12,991.7	10	B.
Propane	C_3H_8	12,027.3	10	Th.
Do	C_3H_8	12,543.0	10	B.
Do	C_3H_8	12,582.0	5,7	
Acetylene	C_2H_2	11,919.7	7	Th.
Do	C_2H_2	11,923.0	10	Th.
Do	C_2H_2	12,112.0	10	B.
Ethylene	C_2H_4	11,858.0	3,10	F. & S.
Do	C_2H_4	11,894.4	7,5	
Do	C_2H_4	11,883.6	10	Th.
Do	C_2H_4	12,154.0	10	B.
Propylene	C_3H_6	11,730.0	10	Th.
Do	C_3H_6	12,045.0	10	B.
Do	C_3H_6	11,717.0	5,7	
Benzol (benzene)	C_6H_6	9,949.0	10	B.
Do	C_6H_6	9,977.5	10	St. & L.
Do	C_6H_6	9,997.0	10	St., Ro. & He.
Benzol (gas)	C_6H_6	10,041.0	10	B. & Og.
Do	C_6H_6	10,096.0	10	St., Ro. & He.
Do	C_6H_6	10,247.4	10	Th.
Naphthalene	$C_{10}H_8$	9,628.0	9,10	St. & L.
Do	$C_{10}H_8$	9,618.7	10	St. & L.
Do	$C_{10}H_8$	9,664.0	10	B. & R.
Do	$C_{10}H_8$	9,700.0	10	B. & Lu.
Do	$C_{10}H_8$	9,718.0	10	B. & V.
Do	$C_{10}H_8$	9,773.0	10	Ru.
Camphor (inactive solid)	$C_{10}HO_{16}O$	9,298.7	10	Lu.
Do	$C_{10}HO_{16}O$	9,291.6	9	St.
Do	$C_{10}HO_{16}O$	9,288.0	9	B.

Nearly all of these results were obtained by burning the substance in oxygen gas in the bomb; but if we examine and compare the heat values obtained by different investigators with the same compound, and note how one author quotes the results of one, and another those of a second, investigator as being the correct ones, we reach but one conclusion, namely, that some one is wrong. Two different results can not both be correct. The differences are in many instances so great that they can not possibly be ascribed to impure substances or ordinary analytical errors due to drying, weighing, etc. But who will take the responsibility of saying that one investigator is right and another wrong? Or that so much of one man's work and so much of the work of some one else is correct? Each of the two men whose names appear most frequently (Stohmann and Berthelot) has a large following. Many will accept Stohmann's results before those of anyone else, and the same may be said of Berthelot; yet there is nothing which indicates that there was some particular fault in the operation of one distinct from the other, for in some cases Stohmann, and in others Berthelot, has the higher figures for the same substance.

Judging from the records of the different investigators, the most that can be said is that with a few substances we have the heats of combustion to within the limits of analytical error, but with the majority only approximately so, and with a few not even that.

Evidently there is need of a revision in the heat values of organic substances so that only the reliable, or at least nearly correct, values should find their way into the tables of text-books, etc., and the faulty ones be dropped. Until such a systematic checking up of the older results by means of the very best and most modern apparatus has been done, the bomb calorimeter should be used freely in all investigations where the heats of combustion play a part, and the values found by actual determinations should be preferred to those obtained or computed from general tables. The bomb thermometer may also to a limited extent serve as a standard with which other thermometers in use may be compared.

VARIATIONS IN DETERMINATIONS ALREADY ON RECORD.

In order to make these figures a little plainer and to put the matter in more compact form I have selected some of the more common compounds from the previous table, and, placing the highest reported heat of combustion of a substance at 100, have shown in the following table the difference between it and the lowest result obtained by some other investigator:

TABLE II.—*Difference between the highest and lowest results on some common compounds referred to in Table I.*

Substance.	Number of investigators.	Difference.	Substance.	Number of investigators.	Difference.
		Per cent.			*Per cent.*
Hydrogen	8	1.86	Cane sugar	9	6.42
Charcoal	4	4.53	Milk sugar	4	6.85
Sulphur	4	4.33	Milk sugar, hydrated	9	7.17
CO to CO_2	5	1.60	Maltose	2	5.13
Hemoglobin	5	1.09	Maltose, hydrated	2	5.35
Milk casein	8	4.10	Cullulose	6	1.40
Egg albumin	4	2.72	Starch	6	2.65
Blood fibrin	7	4.52	Inulin	3	2.75
Peptone	4	7.98	Methyl alcohol liquid	3	1.13
Chondrin	3	8.11	Ethyl alcohol liquid	5	2.83
Urea	6	16.53	Glycerin	3	1.20
Glycocoll	4	2.67	Mannite	5	2.33
Hippuric acid	3	.46	Acetic acid	6	2.11
Asparagin	3	3.31	Palmetic acid	5	1.46
Uric acid	4	4.83	Stearic acid	5	4.80
Fat of swine	5	3.16	Oxalic acid	5	16.08
Fat of oxen	4	3.40	Benzoic acid	6	1.25
Butter fat	6	.57	Methane	4	1.60
Olive oil	7	1.56	Benzol liquid	3	.48
Arabinose	3	.73	Benzol gas	3	2.02
Galactose	2	1.68	Naphthalene	6	1.58
Dextrose	6	1.86	Camphor	3	.12

In chemical-laboratory work, whether it be by advanced students or professional chemists, it is required that the work of the analyst shall be within certain limits of error, varying, naturally, with the nature of the substance analyzed and the method employed. No fixed rule can be laid down as to the limits of error allowed, but for most of the more common substances—such as oxides, carbonates, many ores and clays, etc.—some of which have many ingredients to be

determined, the total of the determinations must come, barring exceptional cases, within, say, about 99.75 per cent and 100.5 per cent, in order to be accepted. The extent to which the results obtained by different analysts on a single ingredient are allowed to vary is very variable. In a determination like that of total nitrogen, for example, the substance containing 18 per cent nitrogen, two analysts should come not farther than about 0.05 or 0.06 per cent apart in the results obtained, except for special reasons. Such a variation as, for instance, between 17.97 per cent and 18.03 per cent nitrogen would be equal to 0.33 per cent difference between the analysts.

Of the 44 cases just cited in Table II the difference between the results obtained by different investigators is below 1 per cent for only five substances. With most of the substances the analysts are several points apart, and in urea and oxalic acid there are differences of over 16 per cent.

That two determinations by the same analyst agree when the same quantity of the sample is used, under exactly the same conditions and manipulations, is no guaranty that the method is perfect or the result correct. If, on the other hand, results agree when charges varying in weight have been used under somewhat varying conditions within the working limits of the method, we feel more sure about their being correct.

CAUSES OF DIFFERENCES IN HEAT DETERMINATIONS.

The method for the determination of heat values of substances can not be considered perfect until work can be done as accurately as is possible in ordinary chemical analyses at least.

From the heat values given we are led to question: What can have caused these differences in the past? What causes differences at present?

Following the directions given in Wiley's Principles and Practice of Agricultural Analysis, Volume III, a number of determinations had been made in this laboratory by means of the apparatus already described, using the commercial oxygen gas found on the market, put up in iron cylinders under very high pressure. The water equivalent of the whole bomb system had been determined by burning cellulose and cane sugar in oxygen under 20 atmospheres' pressure in the bomb, 4,185 calories per gram being the heat value used for the cellulose and 3,955.2 calories per gram for the sugar. The average of a large number of determinations had given the value as 430 grams, and since exactly 2,000 grams of water was used in all cases, the factor was 2,430.

Apparently there was no difficulty in obtaining concordant results when like charges were burned, but with varying charges the work was not satisfactory. The analytical error with a small charge may of

course magnify the percentage error, but, excluding this possibility, it should be possible with a small charge to obtain results indentical with those obtained from a larger charge of the same material. To say that 4,000 to 5,000 calories should be generated in the bomb in order to give good results, and that with only 2,000 calories the work is not satisfactory, is to say that the entire method is unreliable.

IMPURE OXYGEN.

Some difficulties which were experienced in elementary carbon and hydrogen determinations in which the same oxygen was used led to the examination of the oxygen for impurities in the form of combustible gases. It was found beyond a doubt that such impurities were present in the oxygen in quantity sufficient to be reckoned with, and the magnitude of the error caused by them will be referred to further on.

Now arose the questions: To what extent do these combustible gases influence the working of the bomb calorimeter? Is the water value of the bomb, determined by the use of this impure oxygen, correct? Can a correction and the water value be worked out correctly?

TESTING OF OXYGEN.

In order to give the apparatus a severe test and to try to work out an answer to some of these questions, using the impure oxygen itself for the purpose, the following method was adopted: Cellulose was chosen as the chief substance to be burned, and sugar in the form of rock candy was also used. By burning small charges of pure cellulose absorption blocks in the bomb calorimeter, charged with oxygen at various pressures, it was hoped that any increase found with the greater pressure of oxygen would represent the total impurity in the additional amount of oxygen equivalent to the increased pressure, and that, having ascertained the correction for impurities, it could be applied and the water value of the bomb worked out without difficulty. Cellulose, although a very hygroscopic substance, and on that account difficult to handle, was chosen for this work because it ignites readily and burns quickly and completely in a comparatively small excess of oxygen. It represents the main class of substances whose heats of combustion are determined in our work, and its heat value is fairly well established. Sugar, on the other hand, is a substance which does not ignite readily and which burns more slowly, often leaving a trace of unburned carbon even with plenty of oxygen.

It was soon learned that the combustible gases in the oxygen were not oxidized completely, and perhaps never can be fully burned in a bomb calorimeter, but the tests were carried out as planned. The problem was not so simple as at first thought, but it was hoped that the oxidation of the gases referred to would be in proportion to the density of the gas mixture or the heat generated in the bomb. This

is by no means a perfect method, but it may be a means of helping over the difficulty when no pure oxygen or other means for comparison are at hand.

One lot of oxygen (Oxygen I) was tested with both cellulose and sugar in the manner described. A second lot (Oxygen II) was tested only with cellulose. In every instance the cellulose was dried at between 103° and 105° C. to constant weight.

The effect of the impurities may be seen in Tables III to VII, where the corrected rises in temperature will indicate the differences due to more or less oxygen and to the amount of heat generated in the bomb. But before we discuss these results we may examine Table III, where we find the heats of combustion of the various substances worked out as in the course of ordinary routine work, using the water value 430 for the bomb system. This value plus the 2,000 grams of water used makes the factor for the bomb system plus water equal to 2,430 grams.

The column headed "Total computed calories" refers to all the heat generated in the bomb, and includes the heat represented by the substance and the iron wire burned, the nitric acid formed and dissolved, and the heat due to the electric current whenever it failed to ignite the substance instantly.

Varying amounts of oxygen will change the water value of the system; hence in all cases where more or less than 20 atmospheres oxygen was used the temperature rises have been corrected to 20 atmospheres oxygen pressure. For this bomb—of about 360 c. c. capacity—the correction for 1 atmosphere oxygen is ±0.0046 per cent of the observed rise in temperature. Thus, taking for example the first rise referred to in Table III, the rise due to the burning of 0.5092 gram sugar in 10 atmospheres oxygen, corrected to 20 atmospheres oxygen, will be:

	°C.
Observed rise in temperature	0.8488
Correction for 10 atmospheres oxygen	.00039
Corrected rise	.84841

The heat values accepted for the following substances, and used in the computations of the bomb water values given in Table III, are:

	Calories per gram.
Cellulose	4,185.0
Sugar	3,955.2
Naphthalene	9,628.0
Camphor	9,290.0
Benzoic acid	6,322.0

The water values of the bomb as found worked out in Table III have not been used in any computation, but they will indicate how widely the individual values vary from 430—the value used in the calculations of heats of combustion.

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TABLE III.—*Water value of the bomb calorimeter and heat value per gram of substance, worked out by using the water value 430.*[a]

Substance.	Lot of oxygen used.	Oxygen pressure.	Weight of substance.	Total computed.	Rise corrected for oxygen, 20 atmospheres.	Bomb water value.	Calories per gram.
		Atmospheres.	*Grams.*	*Calories.*	°*C.*		
Sugar	I	10	0.5092	2,050.26	0.8484	416.6	3,976.0
		10	.5019	2,013.96	.8352	411.3	3,983.1
		24	.5054	2,038.32	.8493	400.1	4,005.4
		24	.5096	2,046.35	.8558	390.1	4,020.2
		24	1.0000	4,106.14	1.7037	410.0	3,986.6
Cellulose	I	10	.3799	1,617.47	.6671	424.6	4,194.4
		10	.3840	1,628.16	.6746	413.5	4,213.8
		10	.3711	1,571.58	.6484	423.8	4,193.3
		15	.3789	1,604.70	.6678	403.1	4,232.3
		20	.3800	1,609.68	.6734	390.4	4,255.2
		20	.3737	1,584.11	.6604	398.7	4,240.2
		20	.3714	1,574.21	.6558	400.4	4,237.2
		20	.6800	2,868.06	1.1896	410.9	4,218.3
Cellulose	II	10	.4358	1,802.34	.7381	442.0	4,164.2
		10	.4257	1,803.55	.7395	438.7	4,169.8
		24	.4253	1,824.37	.7489	435.9	4,174.5
		24	.4276	1,815.50	.7450	436.8	4,173.4
		24	.6675	2,817.39	1.1579	433.1	4,179.5
		24	1.0035	4,229.14	1.7492	417.7	4,206.4
Naphthalene	II	20	.5274	5,108.42	2.1111	419.8	9,668.9
		20	.5430	5,255.04	2.1785	412.2	9,699.3
Camphor	II	20	.4671	4,360.28	1.7985	424.4	9,311.6
		20	.5034	4,703.37	1.9409	423.3	9,315.8
Benzoic acid	II	20	.6986	4,438.67	1.8390	413.6	6,365.1
		20	.7027	4,473.37	1.8520	415.4	6,360.4

[a] No correction for impurities in oxygen is applied.

These determinations, too few in number for very good averages, were made now and then as other work permitted; hence they cover months of time. A hasty glance over these figures would be enough to condemn the apparatus as being useless for accurate work or the investigator as being unskilled or careless. Of course the analytical errors of the small charges will, as already said, be magnified; hence the duplicates may not always agree closely. Looking a little closer at the table, we notice that all the different groups—that is, those which were treated alike as to quantity of substance and the amount of oxygen—agree fairly well, thus proving that the differences between the groups are not due to careless manipulation. The reason for the disagreements must be sought for elsewhere.

But how are we to interpret the figures, which, in some cases, apparently contradict each other? In the column giving calories per gram we find in the case of cellulose an extreme difference of over 2 per cent in the heat of combustion. Further, we notice that 0.5 gram sugar burned in 10 atmospheres oxygen gave as high results as when 1 gram sugar was burned in 24 atmospheres oxygen. Again, in the case of cellulose in Oxygen I, the smaller charges at 20 atmospheres oxygen gave higher results than the larger charge at the same oxygen pressure, whereas in the case of Oxygen II the opposite is shown.

Another very marked peculiarity in the results is that, with the same factor for the bomb, etc., and the same kind of cellulose, in the work with Oxygen I, all the results on both sugar and cellulose are above the accepted values—sugar as much as 1.6 per cent and cellu-

lose up to 1.64 per cent. In Oxygen II, on the other hand, all the cellulose results, except the one where over 1 gram cellulose charge was used, are below the accepted heat value; but the naphthalene, camphor, and benzoic acid are all above—naphthalene about 0.7 per cent, camphor about 0.3 per cent, and benzoic acid about 0.7 per cent. It should be mentioned here, however, that these substances, while bought as chemically pure, were not tested for impurities before using.

Looking at the column giving the water values of the bomb, we find a corresponding variation, most of the values being below the one used (430), ranging anywhere from 390 to 442.

If a general view is taken of the various results and the behavior of the substances under different conditions, we are convinced that the oxygen contains considerable impurity in the form of combustible gases, for which corrections must be applied. This being the case, the old, apparently too high, water value (430) of the bomb will not be high enough.

CORRECTION FOR IMPURITY IN THE OXYGEN.

Is the correction a constant quantity? Is it of any value to know the total amount of carbon and hydrogen present as combustible gases in the oxygen? These are some of the questions which now concern us as we endeavor to work out the water value of the bomb system, applying the corrections as found for the oxygen and for the amount of heat generated in the bomb.

We turn our attention to Tables IV to VII and examine first the work with cellulose, Oxygen I. From Table IV we learn that between the averages computed to be due to like charges burned in ten atmospheres oxygen pressure and 20 atmospheres there is a slight difference in the rise in temperature in favor of the greater amount of oxygen. This difference does not represent the total impurity in that amount of oxygen, but only the amount which will be oxidized under the specific conditions of so much cellulose and so much oxygen. The difference in rise in temperature, when about 1,600 calories were generated in the bomb, was 0.000665° C. for 1 atmosphere oxygen.

TABLE IV.—*Rise in temperature caused by burning like quantities of cellulose in the bomb calorimeter, in varying amounts of oxygen (Oxygen I).*

Oxygen pressure.	Cellulose.	Fuse wire.	HNO_3.	Total computed.	Rise in temperature.	Rise corrected for oxygen, 20 atmospheres.	Rise due to 1,600 calories.
Atmospheres.	*Grams.*	*Calories.*	*Calories.*	*Calories.*	*° C.*	*° C.*	*° C.*
10	0.3799	17.12	2.60	1,617.47	0.6674	0.6671	0.6599
10	.3840	17.12	1.00	1,628.16	.6749	.6746	.6629
10	.3711	16.48	2.00	1,571.58	.6487	.6484	.6601
15	.3789	16.00	3.00	1,604.70	.6679	.6678	.6658
20	.3800	15.68	3.70	1,609.68	.6734	.6734	.6694
20	.3737	15.68	4.50	1,584.11	.6604	.6604	.6670
20	.3714	16.00	3.90	1,574.21	.6558	.6558	.6665

	°C. rise.
1,600 calories in 20 atmospheres oxygen pressure	0.66763
1,600 calories in 10 atmospheres oxygen pressure	.66098
Difference	.00665
Rise per atmosphere oxygen pressure	.000665

Whether this error is uniform throughout—that is, whether the eleventh atmosphere oxygen, for instance, would show the same error as the twenty-first atmosphere with the same charge—can not be ascertained from these figures. At present we can only assume the error to be uniform.

Is this then the true correction to apply, no matter how large a charge was burned, or will more of the gases be oxidized in the same quantity of oxygen when more heat is generated?

Rock candy, Oxygen I.—In Table V we find a difference in the rise of temperature between 10 and 24 atmospheres oxygen pressure equal to 0.00045° C. per atmosphere when about 2,000 calories are generated in the bomb.

TABLE V.—*Rise in temperature caused by burning like quantities of rock candy in the bomb calorimeter in varying amounts of oxygen (Oxygen I).*

Oxygen pressure.	Rock candy.	Fuse wire.	HNO_3.	Total computed.	Rise in temperature.	Rise corrected for oxygen, 20 atmospheres.	Rise due to 2,000 calories.
Atmospheres.	*Grams.*	*Calories.*	*Calories.*	*Calories.*	*°C.*	*°C.*	*°C.*
10	0.5092	18.08	3.25	2,050.26	0.8488	0.8484	0.8276
10	.5019	16.80	3.15	2,013.96	.8356	.8352	.8293
24	.5054	19.52	4.10	2,038.32	.8491	.8493	.8335
24	.5096	13.16	4.50	2,046.35	.8556	.8558	.8364

	°C. rise.
2,000 calories in 24 atmospheres oxygen pressure	0.83481
2,000 calories in 10 atmospheres oxygen pressure	.82847
Difference	.00634
Rise per atmosphere oxygen pressure	.00045

Sugar, as has been said, does not always burn completely. Frequently a hardly weighable amount of carbon may be seen on the platinum capsule, a very small spot perhaps, yet it is an indication of incomplete combustion of the carbon itself and of the possibility that at least traces of intermediate partially oxidized products may be found.

Cellulose, Oxygen II.—In Table VI we find the results obtained with cellulose and another lot of oxygen. Here 1,800 calories produced in oxygen at 10 and 24 atmospheres pressure, a difference in temperature of only 0.00007° C. per atmosphere, which is within the limits of analytical error.

TABLE VI.—*Rise in temperature caused by burning like quantities of cellulose in the bomb calorimeter in varying amounts of oxygen (Oxygen II).*

Oxygen pressure.	Cellulose.	Fuse wire.	HNO_3.	Total computed.	Rise in temperature.	Rise corrected for oxygen, 20 atmospheres.	Rise due to 1,800 calories.
Atmospheres.	*Grams.*	*Calories.*	*Calories.*	*Calories.*	°C.	°C.	°C.
10	0.4258	17.12	3.25	1,802.34	0.7384	0.7381	0.7371
10	.4257	19.20	2.80	1,803.55	.7404	.7395	.7386
24	.4253	21.12	5.00	1,824.37	.7488	.7489	.7389
21	.4276	21.44	4.55	1,815.50	.7449	.7450	.7387

	° C. rise.
1,800 calories in 24 atmospheres oxygen pressure	0.73881
1,800 calories in 10 atmospheres oxygen pressure	.73778
Difference	.00103
Rise per atmosphere oxygen pressure	.00007

We have reason to believe, however, judging from the determinations referred to in Table III that this oxygen supply also was not pure, and hence we take up the question asked before: What effect has increased heat production upon the oxidation of these combustible gases?

For some of the following comparisons I must depend upon single determinations, which in itself is not very satisfactory; but since no more of the same oxygen is at hand for further work I must take for granted that the determinations are correct.

TABLE VII.—*Comparison of observed rise in temperature due to the large and the calculated rise due to the smaller charges of a substance burned in the same quantity of oxygen.*

Substance.	Lot of oxygen used.	Oxygen pressure.	Weight of substance.	Computed total.	Rise.	
		Atmospheres.	*Grams.*	*Calories.*	°C.	
Sugar	I	24	1.0000	4,106.14	1.70366	Observed.
		24	.5075	2,042.33	1.71396	Calculated.
				2,063.81	− .01020	Difference.
Cellulose	I	20	.6800	2,868.06	1.1896	Observed.
		20	.3750	1,589.30	1.1967	Calculated.
				1,278.76	− .0071	Difference.
Cellulose	II	24	1.0035	4,229.14	1.7492	Observed.
		21	.4265	1,819.93	1.7359	Calculated.
				2,409.21	+ .0133	Difference.
		24	.6675	2,817.39	1.1579	Observed.
		21	.4265	1,819.93	1.1564	Calculated.
				997.46	+ .0015	Difference.

In Table VII we find that when 1 gram of sugar was burned in 24 atmospheres oxygen, 4,106.14 calories of total heat being generated in the bomb, the rise in temperature of the bomb system was found to be 1.70366° C. The average rise in temperature found when 0.5075 gram of sugar was burned, or 2,042.33 calories of total heat was gene-

rated in the bomb, in the presence of 24 atmospheres oxygen, was 0.8525° C., and according to that the generation of 4,106.14 calories should have caused a rise of 1.71396° C. instead of 1.70366° C., as found when 1 gram was burned. The difference, therefore, is a minus of 0.0102° C. This indicates that, of the impurities in this particular oxygen, more were oxidized in proportion as the charge of sugar was reduced. Hence the correction referred to in Table V should not be increased in proportion to the increase in the amount of substance used.

With cellulose in Oxygen I a charge of 0.6800 gram, which, plus wire, etc., was equivalent to 2,868.06 calories total heat generated, gave a rise of 1.1896° C. instead of 1.1967° C. as it should have done according to the results upon the smaller charges. Here is also a minus difference of 0.0071° C., showing that this oxygen behaved the same with these two different substances. The combustible gases present in the oxygen must accordingly be of an easily combustible nature, comparatively speaking, when the increase in heat has no effect upon them above that of the lesser heat.

Next we examine the results obtained with different amounts of cellulose in Oxygen II. Here we see not a decrease, but a very marked increase in the oxidation of combustible gases with increase in heat evolved. A charge of 0.6675 gram cellulose, or a total heat production of 2,817.39 calories, gave a rise in temperature of 1.1579° C., which is 0.0015° C. above what it should have been according to calculation from the results of the smaller charge of 0.4265 gram cellulose, equal to 1,819.93 calories total heat. When 1.0035 grams cellulose was burned there was a difference of 0.0133° C. above the calculated result. This difference in behavior of the two oxygen supplies toward larger charges of the substances burned indicated a difference in composition of the combustible gases in the oxygen. In Oxygen I the gases were apparently more readily oxidized than in Oxygen II, and therefore more of them burned with the small charges in proportion to what burned with the larger. The opposite would then be true of Oxygen II. Unfortunately no further and more definite proof can be given, since no qualitative tests were made of the gases. As to the impurities in Oxygen I being different from those in Oxygen II, there can be no doubt. In the first lot a strong, peculiar, disagreeable odor was noticed, and when the gases passed through pumice stones saturated with H_2SO_4 a slight yellow coloration was noticed for a short distance. Oxygen II had no such disagreeable odor and did not color the pumice stone as did Oxygen I.

According to analyses made by one of the assistant chemists of the experiment station, Oxygen I contained 0.0355 per cent of hydrogen and 0.0150 per cent of carbon by weight, while Oxygen II contained 0.0335 per cent of hydrogen and 0.0150 per cent of carbon.

These results show that there must have been considerable free hydrogen present.

Not knowing the composition of the gases referred to, we may, for the sake of obtaining at least an approximate calorific value, assume that all the carbon is present as marsh gas, and that the excess of hydrogen is free hydrogen. Thus we have in Oxygen I 0.02004 per cent CH_4 and 0.01446 per cent free H_2, and in Oxygen II 0.02004 per cent CH_4, and 0.01346 per cent free H_2.

With 20 atmospheres oxygen, or in round numbers 10 grams of oxygen, these gases would represent in Oxygen I 73 calories, equivalent to 0.0299° C. rise, and in Oxygen II 69 calories, equivalent to 0.0283° C. rise.

In none of the determinations referred to with the above-mentioned oxygen was more than about 45 per cent of these figures reached, which can be seen in Table IV, where the correction for the impurities in 20 atmospheres oxygen equals 0.0133° C. This indicates plainly that only a part of the combustible gases mixed with the oxygen can be oxidized in the bomb.

RISE IN TEMPERATURE CORRECTED FOR HEAT DUE TO IMPURITIES IN THE OXYGEN.

In Table VIII following are given the corrected figures for the rise in temperature, also the values computed for the bomb water value and for the heats of combustion of the substances, respectively. The corrected figures for the rise in temperature are obtained by using the results of Tables IV to VI. Thus the corrections used for the sugar and cellulose burned in Oxygen I are the differences found in Tables IV and V. No account has been taken of any increase in total heat formed in the bomb by use of larger amounts of material with Oxygen I.

For the smaller charges of cellulose burned in Oxygen II the differences found in Table VI have been used, and for the larger charges the increase in rise of temperature actually observed (Table VII) has been added to the first-mentioned correction. Thus, where 0.4253 gram cellulose was burned in Oxygen II the correction will be $0.00007° \times 24 = 0.00168°$ C. For the charge of 0.6675 gram cellulose the correction will be $0.00168° + 0.0015°$ C., and for the largest amount of cellulose burned the correction equals 0.0151° C.

To all determinations of the other substances—naphthalene, camphor, and benzoic acid—where the total heat was a little higher than it was with the cellulose charge last mentioned, the same correction, 0.0151° C., has been applied.

The heats of combustion were computed by using the bomb water value 439.2. This value is the average of those found for cellulose, naphthalene, camphor, and benzoic acid with Oxygen II. The average of all the results in Table VIII would be 437.8, but the values obtained

with Oxygen I were not used on account of the sugar and cellulose not agreeing very closely.

TABLE VIII.—*Water value of the bomb calorimeter, and heat value per gram substance, worked out by using the new water value, 439.2, found after applying the corrections for the impurities in the oxygen.*

Substance.	Lot of oxygen used.	Oxygen pressure.	Weight of substance.	Total computed.	Rise corrected for oxygen per 20 atmospheres.	Bomb water value.	Calories per gram.
		Atmospheres.	*Grams.*	*Calories.*	°*C.*		
Sugar	I	10	0.5092	2,050.26	0.8439	429.5	3,969.7
		10	.5019	2,013.96	.8307	424.4	3,976.4
		24	.5054	2,038.32	.8385	430.9	3,969.0
		24	.5096	2,046.35	.8450	421.7	3,984.2
		24	1.0000	4,106.16	1.7031	411.0	4,001.7
Cellulose	I	10	.3799	1,617.47	.6605	449.0	4,188.9
		10	.3840	1,628.16	.6678	438.1	4,186.9
		10	.3711	1,571.58	.6418	448.7	4,168.7
		15	.3799	1,604.70	.6578	439.5	4,184.8
		20	.3800	1,609.68	.6601	438.6	4,158.6
		20	.3737	1,584.11	.6471	448.0	4,170.1
		20	.3714	1,574.21	.6425	450.2	4,166.4
		20	.6800	2,868.06	1.1834	423.6	4,212.6
Cellulose	II	10	.4258	1,802.34	.7373	444.5	4,178.0
		10	.4257	1,803.55	.7388	441.2	4,181.5
		24	.4253	1,824.37	.7472	441.7	4,180.5
		24	.4276	1,815.50	.7433	442.5	4,179.0
		24	.6675	2,817.39	1.1548	439.7	4,184.1
		24	1.0035	4,229.14	1.7341	438.8	4,185.7
Naphthalene	II	20	.5274	5,108.42	2.0960	437.2	9,635.6
		20	.5430	5,255.04	2.1634	429.1	9,668.3
Camphor	II	20	.4671	4,360.28	1.7834	444.9	9,268.1
		20	.5034	4,703.37	1.9258	442.3	9,277.9
Benzoic acid	II	20	.6986	4,438.67	1.8239	433.6	6,336.6
		20	.7027	4,473.37	1.8369	435.3	6,332.1

The corrected results in Table VIII agree fairly well among themselves, and even where the conditions for determinations differed so widely from the ordinary they approach the heat values generally accepted for the substances used. This certainly could not be said when the impurities were not considered, as was seen in Table III, where a higher value was used than the average of the water values given in that table. From all that has been said on this topic we learn that, at best, the determination of the hydrothermo equivalent, or water value, of the bomb with impure oxygen is no easy task, nor can it be very satisfactory. Hence the method explained can be recommended for use only where no pure oxygen—i. e., oxygen free from combustible gases—can be obtained.

FORMATION OF NITRIC ACID IN THE BOMB CALORIMETER DURING COMBUSTION.

The formation of HNO_3 in the bomb has already been alluded to, also that correction must be made for the heat represented by the HNO_3 solution.

In the bomb there is always present more or less free nitrogen, and a portion of it is always oxidized, varying in quantity according to the nature of the substance burned, the total heat generated, and the quantity of nitrogen in the bomb. This quantity of HNO_3, which

appears to be constant for specific conditions, I propose to designate, for convenience, "bomb nitric acid," meaning thereby the HNO_3, expressed in calories, which would be formed in the bomb from free nitrogen during the combustion of a specified substance under specified conditions. Table IX, following, gives us an idea as to the value of this quantity for the oxygen used. This quantity, however, represents only a very small portion of the free nitrogen present in the bomb.

TABLE IX.—*Formation of HNO_3 in the bomb calorimeter during combustion of nonnitrogenous substances.*

Substance.	Determinations.	Oxygen.	Weight of substance.	Total heat.	HNO_3.	HNO_3 per 1,000 calories.
	Number.	*Atmospheres.*	*Grams.*	*Calories.*	*Calories.*	*Calories.*
Cellulose	6	24	0.5481	2,335.2	6.74	2.89
Do	7	20	.6550	2,763.9	6.50	2.35
Do	6	10	.3946	1,677.4	3.01	1.79
Sugar	4	24	.7538	3,016.4	6.13	2.04
Do	7	20	1.2437	5,019.7	9.87	1.97
Do	2	10	.5056	2,019.0	3.20	1.58
Naphthalene	2	20	.5352	5,182.2	8.82	1.70
Camphor	2	20	.4853	4,531.9	7.70	1.70
Benzoic acid	2	20	.7007	4,454.6	7.55	1.70

In the last column of the foregoing table we see that this indifferent gas nitrogen behaves very much like the combustible gases present as impurities in the oxygen, namely, with an increase in quantity of oxygen, accompanied by an increase of free nitrogen, more nitrogen was oxidized. The individual determinations also showed a tendency to increased nitrogen oxidation with an increase in amount of substance burned.

For cellulose and the class of substances which it represents, such as feeds and feces, we can use, without introducing any appreciable error in the following calculations, a correction of 2.4 calories for each 1,000 calories total heat at 20 atmospheres oxygen pressure for the HNO_3 formed. For sugar and substances which would burn more like sugar than cellulose, such as gelatin, dried urine, milk, etc., we may use 2 calories per 1,000 calories total heat as the corresponding correction for the HNO_3 formed.

OXIDATION OF COMBINED NITROGEN TO NITRIC ACID.

It is generally assumed that the combined nitrogen in organic substances is set free as elementary nitrogen during a combustion. But in view of what has already been said we may be led to question whether all, or at least part, of this nitrogen may not also be burned to HNO_3, perhaps even more readily so than the free nitrogen gas. It will be my object to take up the question of nitrogen of the substances to be analyzed, to see how much of this nitrogen is oxidized during a combustion, and what effect, if any, this will have upon the general results.

To illustrate the points which I want to bring out in this connection, and to make the tabulated figures more reliable, I have collected and taken the average of a large number of figures from work done at this station by Messrs. Norris and Carpenter on feeds, excreta, etc., the heats of combustion of which were mostly used in connection with the nutrition investigation experiments with cattle by means of the respiration calorimeter, referred to earlier in this paper. These data have served as the chief basis for the computations set forth in Table X. The substance in each charge was either a nitrogenous compound or mixed with one, so that in each case nitrogen was present in a combined form. From such a variety of substances we may expect to find some differences brought out as to the behavior in regard to the nitrogen, if any difference exists.

TABLE X.—*Average HNO_3 formed during the combustion of various nitrogenous substances in the bomb calorimeter.*

Substance.	Single determinations.	Average charge.	Total heat.	Nitrogen in charge.	Bomb HNO_3.	HNO_3 found.
	Number.	*Grams.*	*Calories.*	*Grams.*	*Calories.*	*Calories.*
Clover hay	79	1.0178	4,355.8	.0183	10.45	5.68
Grain feed	16	1.0031	4,508.9	.0342	10.82	9.51
Corn meal	18	1.0046	4,252.9	.0167	10.21	9.38
Linseed meal	11	1.0110	4,923.4	.0616	11.80	13.92
Feces	70	1.0144	4,454.3	.0191	10.69	10.33
Hair and dandruff	17	.8218	3,828.0	.0601	7.66	34.10
Gelatin	5	.6601	2,671.4	.1188	5.34	12.42
Alcohol+Gelatin	16	.6819 .2006	4,392.0 965.6	.0349	12.86	17.81
Urine+Much cellulose	20	4.7571 .6623	1,182.8 2,771.7	.0462	7.91	.00
Urine+Little cellulose	29	7.5178 .0508	1,548.3 212.8	.0478	3.52	1.78
Milk+Cellulose	9	1.4648 .6596	1,103.9 2,760.4	.0079	9.27	9.22
Milk alone	9	4.0354	3,327.9	.0225	6.66	9.17

In the above table we find, besides the amount of the sample used and the total heat produced in the bomb, the total nitrogen in the charge taken, the bomb nitric acid as calculated by using the values obtained in Table IX, and the actual HNO_3 found. It was assumed that the acidity in the bomb was due entirely to HNO_3. The figures represent the averages of numerous closely agreeing determinations; in the case of hay, 79 single determinations. It may be stated here that the nitrogen represented by 1 calory is equal to 0.00098 gram, or to 0.004406 gram HNO_3.

From these figures we learn first of all that the nitrogen behaves differently in different substances. Hair and dandruff, for instance, gave 4.5 times as much nitric acid as was due to the oxidation of the atmospheric nitrogen in the bomb, whereas gelatin, which contained about twice as much total nitrogen in the sample, gave not much more than one-third as much nitric acid as did the hair and dandruff, and only 2.3 times as much as the bomb nitric acid called for. In the case of urine plus considerable cellulose there was, strangely enough, no

nitric acid found at all, yet about 8 calories should have been formed from the free nitrogen of the bomb alone. But with urine plus a little cellulose a small amount of HNO_3 was found. Naturally, one would expect more where more cellulose was used. These variations may introduce errors into the computations of the heat values of the substances, and in order to see the extent of these variations more clearly, and perhaps the probable errors, I have presented the results in another form in Table XI.

TABLE XI.—*Errors due to the oxidation of nitrogen.*

Substance.	Per cent found of total HNO_3 possible.	Nitrogen of sample oxidized to HNO_3.	±Deviations from bomb HNO_3.	Errors of total calories of sample.
		Per cent.	*Calories.*	*Per cent.*
Clover hay	19.47	0.0	− 4.77	0.11
Grain feed	20.80	.0	− 1.31	.03
Corn meal	34.37	.0	− .83	.02
Linseed meal	18.61	3.37	+ 2.12	.04
Feces	34.18	.0	− .36	.01
Hair and dandruff	49.56	43.02	+26.44	.70
Gelatin	9.80	5.83	+ 7.08	.27
Alcohol+gelatin	46.97	19.75	+ 4.95	.11
Urine+much cellulose	.0	.0	− 7.91	.69
Urine+little cellulose	3.40	.0	− 1.74	.11
Milk+cellulose	56.39	.0	− .05	.00
Milk alone	30.91	10.91	+ 2.51	.08

The bomb nitric acid plus the nitric acid represented by the oxidation of the total nitrogen of the charge is called 100, and in the first column of this table are found, expressed in percentages, the amounts formed of this possible HNO_3. In the second column is given the percentage of the nitrogen of the sample oxidized to HNO_3. The last two columns give the variations of nitric acid found from the bomb HNO_3, and the percentage of the total heat values represented by this number of calories, as calculated from the determinations.

Several plus and several minus deviations from the computed bomb nitric acid are noticed in the preceding table. The minus signs force us to question: Was the full amount of bomb HNO_3 not formed, or was it formed and did it disappear again, changed into some other compound? The work done is not enough to answer this question fully, but I am strongly inclined to believe that the nitric acid was formed, but immediately on forming was changed into some other combination, probably through the influence of the ash ingredients.

In the bomb the nitric acid is found dissolved in the moisture which is condensed on the sides of the bomb. Here it may be mentioned that in transferring the nitric acid from the bomb to a beaker for titration care should be taken not to wash out the platinum capsule or add the ash to the rinsing. Often the ash is very strongly alkaline and would make the whole solution alkaline, which would be the same as having a minus quantity of acid formed—an impossibility.

This finding of the nitric acid and water together on the sides of the

bomb would seem to indicate that the nitric acid is formed as a gas, and, together with the water in gaseous form, is expelled or driven from the seat of the great chemical activity or point of combustion to unite and condense with the moisture on the cool sides of the bomb. But this can not always be the nature of the combustion, judging from the sample of urine plus considerable cellulose. Here also the water was condensed on the sides of the bomb, and from the cellulose alone there should have been several calories HNO_3 dissolved in it, but the water was neutral. The ash, on the other hand, was decidedly alkaline. Where the urine was burned with but a small quantity of cellulose one-half of the bomb HNO_3 was found in the water. Here, too, the ash was alkaline. Nitric acid, it seems, can not be formed by the action of the flame and heat on nitrogen away from the ash or skeleton of the substance burned, but must be formed in the capsules holding the substance at the very point where the heat first attacks the compound, the place of greatest chemical activity. We can imagine that in a remarkably short time numberless chemical changes must take place at that point. The nitric acid does not leave this seat of action when there is some attraction strong enough to hold it. In the case of urine and other substances such an attraction seems to be in the ash, and hence little or none of the nitric acid escapes with the other gases formed to the sides of the bomb. The attraction referred to can hardly be anything but the chemical affinity of the alkalies of the ash, which unite with the acids formed, thus holding at least part if not all of them. In this we have an explanation of how it is possible to have less than the bomb HNO_3, since ash with alkaline reaction will prevent nitric acid from being dissolved in the water and perchance prevent in part its very formation.

Eight ashes left by the combustion of urine plus a little cellulose were analyzed for nitrogen, and the average of the results gave the equivalent of 1.1 calory HNO_3, which represents most of the 1.74 calories of missing nitric acid, as shown in Table X. Unfortunately, only these 8 ashes were saved for nitrogen determination. What the nitrogen compounds were in the ash was not determined, nor do we know anything about what part of the missing nitric acid was present in the ash, in the case of the urines, where all was missing, none being dissolved in the water in the bomb.

PROBABLE ERROR DUE TO DISAPPEARANCE OF NITRIC ACID.

Taking for granted that the plus values in the table refer to the total nitric acid formed, and that not any of it has united with anything else, the plus then does not mean an error, since all the nitric acid formed is measured and accounted for in the calculations. But the minus or missing nitric acid is in all probability always an error which would be greater or less than the values given in the last column, according to the nature of the combination formed. Thus

errors are liable to be introduced when, in the operation of the bomb and computations of the results, the acidity in the solution titrated against NaOH solution is assumed to be HNO_3, and therefore the amount of heat represented by it always subtracted from the total heat generated in the bomb.

There are other acids formed in the bomb besides nitric acid, and directions for the manipulation of the bomb calorimeter should make specific mention of this fact and explain how they should be considered, so as not to introduce any error. They are not in any way equivalent to HNO_3, and should therefore not be treated as such. The writer has in mind especially the H_2SO_4.

It is generally accepted that in a complete combustion of a nitrogenous organic substance the nitrogen returns to free nitrogen and oxidizes only under extraordinary conditions such as may be produced by a powerful electric spark, or which exists in the bomb calorimeter where the combustion takes place in the presence of large excess of oxygen, etc. For this reason any heat caused by the formation of HNO_3 must be subtracted from the total heat generated in the bomb.

With sulphur compounds it is different. The natural combustion product of sulphur is the acid, and hence any heat produced by the formation of H_2SO_4 belongs to the compound and should not be subtracted. Especially is this true when the bomb results are to be compared with the combustions of organic substances as they take place in the animal body. Part or all of the sulphuric acid may be held in the form of salts in the ash, but as the ash is practically an unexplored field, it will not be touched upon at all at this time.

Whether the H_2SO_4 is counted in as HNO_3 or not will at times make a great difference in the final results. This may be seen very clearly from some work which the writer did upon dandruff and hair (brushed off a steer at the daily cleaning), upon pure hair, and upon two samples of steer urine.

The results so far as they bear upon this point are found in Table XII.

TABLE XII.—*Difference in the heat values found when the total acidity is regarded as HNO_3 and when the H_2SO_4 has been subtracted.*

Substance.	Charge.	Acid solution titrated against NaOH solution.			Calories per gram substance.		Difference.
		Total alkali.	Due to H_2SO_4.	Difference HNO_3.	Acidity called HNO_3.	Titration corrected for H_2SO_4.	
	Grams.	*c. c.*	*c. c.*	*Calories.*			*Per cent.*
Brushings (dandruff and hair)	1.0236	68.94	62.98	5.96	4,052.4	4,113.0	1.48
Do	.8959	59.79	58.88	.91	4,048.7	4,125.7	1.87
Do	.8809	59.62	58.27	1.35	4,066.6	4,132.7	1.60
Hair	.9133	49.94	38 54	11.40	5,180.2	5,221.4	.79
Urine	7.2462	1.60					
Do	6.1216	1.65	1.1	3.97	153.36	153.42	.04
Do	6.0444	1.82					
Do	7.6021	2.92					
Do	7.8134	3.19	3.1	6.37	175.6	175.73	.07
Do	8.4447	3.36					

These few determinations will suffice to show that a very large error may be introduced by the H_2SO_4. In the case of urine the error introduced by reckoning sulphuric acid as nitric acid is small, but with the hair it reached about 0.8 per cent, and in the case of the epidermic tissue, dandruff, etc., which is richer in sulphur, the error was in one instance about 1.9 per cent.

CAUSE OF INCOMPLETE COMBUSTION.

The shape and size of crucible, or capsule, in which the substance is burned may influence the combustion.

Owing to inability to watch the process of the combustion in the bomb, the general opinion, gained perhaps from the observations of explosives, is that the combustion in the bomb calorimeter is very sudden and violent, in nature like an explosion in the free air. This, however, is not correct. The time of combustion varies with the nature of the substance, but, with the materials mentioned in the previous tables, only by a very few seconds. It is of a very short duration, but by no means an instantaneous flash. The supposed violence, implying that the flash fills the bomb, has absolutely no foundation and would not happen except when the oxygen contains a considerable percentage of highly combustible gases. To prove the correctness of this statement direct tests were made as follows: Small pieces of filter paper, about one-fourth inch square, were fastened by one edge to the sides, top, and bottom of the bomb by means of paste, and allowed to dry. In one trial the burning of a small charge of cellulose did not affect the few pieces of filter paper which were fastened on the top and on the bottom of the bomb. After that a more complete test was made by fastening three pieces to the top, one at the center of the bottom, and ten distributed on the sides of the bomb; four of them about opposite the top of the capsule, four nearer the top, and two nearer the bottom. The charge was 1 gram powdered rock candy plus a little naphthalene, burned in 20 atmospheres oxygen. The test resulted in two of the three pieces on the top being burned, the third one showing in one corner a trace of brown as when paper has been held near strong heat. All the rest were absolutely untouched. Hence, the flames may at times reach the top, and perhaps more seldom the sides, though the distance is much shorter. With more oxygen the flame very likely would not even have reached the top of the bomb.

It is a known fact that fire will put itself out in a closed room, even before the oxygen is fully consumed. If this is true in a room, might it not also be true in a deep capsule surrounded by plenty of oxygen? To have some light shed upon this question, and to be able to decide in favor of some one of the different shaped capsules used, the follow-

ing tests were made: A wide-mouthed bottle of 1,500 c. c. capacity was filled with oxygen, and the crucible, attached to a wire fastened in the cork, was let down in the bottle, and the substance ignited by means of an iron fuse wire as in the case of the bomb combustion, and the burning watched. The substances burned were filter paper (cellulose), cut in disks and laid on the bottom of the crucible, and powdered sugar (rock candy). After combustion the ordinary test was made for the oxygen by means of a glowing splinter of wood. In all cases there was a large excess of oxygen, since the large cork could be removed and the splinter plunged in and ignited several times in succession.

In the following table, which gives the results of the tests, crucible No. 1 was a large nickel crucible, $1\frac{5}{8}$ inches in diameter at the top and $1\frac{7}{16}$ inches deep. Crucible No. 2 was a small nickel crucible, $\frac{7}{8}$ inch in diameter by $\frac{1}{16}$-inch deep. Crucible No. 3 was the same as No. 2, perforated, and crucible No. 4 was the same as No. 3 with the holes enlarged. A small piece of cellulose, not weighed, was put under the sugar in the crucible in one case to facilitate the combustion. The time which the substance stood in the bottle before ignition was noted, as well as the length of time it continued to burn. The last column in the following table gives the unburned residue:

TABLE XIII.—*Powdered sugar and cellulose burned in different shaped crucibles in oxygen under atmospheric pressure.*

Substance.	Crucible.	Weight of substance.	Time before ignition.	Time of combustion.	Unburned residue.
		Gram.	*Minutes.*	*Seconds.*	*Gram.*
Cellulose	1	0.2190	30	60	0.0000
Sugar	1	.2675	5	75	.0077
Do	2	.2454	5	180	.0081
Cellulose	2	.1890	5	165	.0026
Sugar	3	.2582	8	195	.0122
Do	4	.2132	90	75	.1609
Sugar and cellulose	4	.2037	5	60	.0060
Cellulose	4	.1585	15	40	.0002

In only one instance did the substance burn without leaving any unburned residue of carbon. There was a marked difference between the two substances in the way they burned, the sugar taking longer time and leaving a great deal of unburned matter. A number of holes were made near the bottom of the small crucible. During the burning some of the holes became coated over with a film of charred material, the flame remained smaller, and the circulation of the gases, i. e., of oxygen, to the burning substance was lessened. When the holes were enlarged these last-mentioned hindrances were magnified and the sugar burned only in part, most of it was left untouched by the small flame, and in one spot it was not even fully melted. It is possible that in this case some of the oxygen might have leaked out on standing, but after

the combustion there was enough left in the bottle to allow the glowing splinter to burst into flame several times. When the sugar rested on a small piece of filter paper the combustion of the sugar was more nearly complete, and filter paper alone was practically completely burned in crucible No. 4.

The figures of the table, as well as the actual behavior of the combustion, indicate the shape of the larger crucible, which was very much broader at the top than at the bottom, as being the best. The combustion itself, or we may say the supply of oxygen to the burning points, was more uniform with the larger and more intermittent with the smaller crucible. A good start, and much heat quickly generated, are factors which undoubtedly contribute much to make a combustion complete, but these may not in the least change the conclusion reached as to the shape of the crucible or capsule best suited for the work.

ALCOHOL HEAT VALUE.

Time did not permit me to take up the question of alcohol heat value as fully as I desired, hence at this time I shall make mention of only a few points which have come up in connection with the determination of heat of combustion, and make some suggestions which may at least be of practical value.

Alcohol being a volatile liquid it can not be satisfactorily burned in an open dish, but must be inclosed in a receptacle from which it can not evaporate, and gelatin capsules of known heat value are generally used for this purpose. The alcohol charge should never be weighed out by difference—i. e., by weighing the bottle—but the actual amount placed in the capsule should be weighed. The reason for this is to make sure that there is no evaporation. Unless the capsule with the alcohol is weighed a little evaporation may not be noticed, and if the capsule is not tight enough to hold the alcohol while it is being weighed it is not fit for the work. A little evaporation of alcohol from the capsule in the bomb will always cause the results to come too low, since alcohol vapors are not fully burned. To insure complete combustion of the alcohol and the gelatin the capsule may be filled with clean, ignited asbestos to absorb the alcohol.

Another way to obtain good combustions of the alcohol and gelatin, though not so simple as the gelatin-capsule method, is to make use of a tubular platinum capsule, about one-fourth of an inch in diameter, having perforated sides and bottom. This platinum capsule is coated with a mixture of the best gelatin with about 10 per cent of glycerin and water, all gently heated. The coating is allowed to dry, and the weight of the gelatin mixture is ascertained. Separate portions of the mixture are dried and analyzed for the heat value. This gelatin-coated capsule can be used with or without asbestos. Caps can be made of the same material to fit tightly over the end, or inverted, used

as plugs. It requires less gelatin to coat such a capsule and make it alcohol tight than is found in the ordinary gelatin capsules used.

The weight of all gelatin capsules, etc., should be taken when the the material is dry, and this weight should be used in correcting for the heat of combustion of gelatin. But before using they should have been exposed to room conditions for a considerable time, else there is no constancy about them when they have to be reweighed and filled with alcohol.

ALCOHOL DETERMINATION USED FOR TESTING THE RESPIRATION CALORIMETER.

This was absolute alcohol diluted with distilled water, and hence the first step was to obtain its specific gravity. Two pycnometers were used and the specific gravity was taken at 15.6° C., as follows:

	No. 1.	No. 2.
	Grams.	*Grams.*
Pycnometer, plus distilled water	77.2663	87.2591
Pycnometer, empty	27.2385	37.2259
	50.0278	50.0332
50 cc. air	.05894	.05894
Water	50.08674	50.09214
Pycnometer, plus alcohol	68.4121	78.4056
Pycnometer, empty	27.2385	37.2259
	41.1736	41.1797
50 cc. air	.05894	.05894
Alcohol	41.23254	41.23864

No. 1. 41.23254÷50.08674=.823222 specific gravity.
No. 2. 41.23864÷50.09214=.823255 specific gravity.

Average, =.823238 specific gravity.
According to Squibb, at 15.6° C.
0.82755 specific gravity=88.0 per cent pure alcohol.
.81684 specific gravity=92.0 per cent pure alcohol.

Difference, .01071 specific gravity= 4.0 per cent pure alcohol.
0.82755 =88.0 per cent alcohol.
.823238= unknown alcohol.

.004312

0.01071 : 0.004312 :: 4.0 : X X=1.6105 per cent.
Hence 88.0+1.6105=89.611 per cent ethyl alcohol.

DETERMINATION OF HEAT OF COMBUSTION.

Using the old water value of the bomb and without any correction for oxygen, two determinations of the capsule gelatin gave an average of 4,871 calories per gram, and the average of three determinations of the alcohol gave 6,458.7 calories per gram, or 7,207 calories per gram pure alcohol. Applying the correction found for impurities in oxygen by burning 1 gram cellulose, and using the corresponding water value of the bomb, the average for the gelatin was 4,860 calo-

ries per gram, and for the alcohol 6,447 calories per gram, or 7,194 calories per gram pure alcohol.

A sudden jar of the bomb caused one capsule containing alcohol to fall to the bottom of the bomb. It was ignited, and the determination was carried through as usual, but only 6,949.8 calories per gram pure alcohol was measured—that is, 3.4 per cent less than the above average. Upon opening the bomb there was found a black spot and some yellowish oily liquid at the bottom, and a strong, very peculiar odor mixed with odor of alcohol was noticed, thus showing incomplete combustion very decidedly. Another charge of alcohol which had remained in the capsule in the bomb for several hours before ignition gave 7,091 calories per gram pure alcohol. Here, where there was opportunity for evaporation, the heat obtained was less than the average of the three other determinations.

These observations are sufficient to show that to obtain correct values great care must be taken when volatile substances are to be burned in the bomb.

One or two questions which may possibly prove to be of some importance in connection with this work will be considered briefly.

These questions concern the contents of the bomb before and after combustion, and their influence upon the measurement of the heat, namely, the influence which the changes in the contents have upon the water value of the bomb, and the quantity of heat held by these various compounds formed and not accounted for.

In the following calculations I shall use the values for specific heats, etc., as given below:

Per unit weight:

Cane sugar	=0.301 specific heat.
Water	=1.000 specific heat.
O_2	= .2175 specific heat.
CO_2	= .1875 specific heat.
O_2 1 liter	=1.4298 gram.

To illustrate these problems and for the sake of simplicity we shall consider one example, leaving out all of the minor things which would complicate the calculations. Thus, we have a bomb of 360 c. c. capacity. In the bomb, before combustion, are 1 gram cane sugar and 20 atmospheres pure oxygen, all at 20° C. What changes take place when the sugar is burned, and what are their significance?

According to the weight and specific heat of the substances in the bomb, they represent a certain mass of water at the same temperature; also, a definite quantity of heat is held by them, which may be expressed in calories. Twenty atmospheres oxygen would then be—

20×360 c. c.=7,200 c. c. oxygen.
7,200×1.4298 (weight of 1 liter oxygen)=10.29456 grams oxygen.
10.29456×0.2175 (specific heat)=2.239 grams water.
1 gram cane sugar ×0.301 specific heat=0.301 gram water.

Hence the substances in the bomb represent—

Oxygen	2.239 grams H_2O
Sugar	.301 grams H_2O
Total	2.540 grams H_2O

The sugar burns to CO_2 and H_2O, and after the combustion of 1 gram sugar we find 0.5793 gram water and 1.5426 gram CO_2.

1.5426 grams $CO_2 \times 0.1870$ specific heat=0.288 gram water.
10.29456—1.1219=9.1727 grams O_2, and $\times 0.2175$=1.933 grams water.

Thus in the bomb after combustion we have—

Oxygen equivalent to	1.933 grams H_2O
Carbon dioxide equivalent to	.288 gram H_2O
Water	.5793 gram H_2O
Total	2.8003 grams H_2O
After combustion	2.8003 grams water
Before combustion	2.5400 grams water
Difference (increase)	.2603 gram water

The whole bomb system therefore has changed to an extent equivalent to 0.2603 gram water during the combustion. This is equal to 0.011 per cent of the total bomb water value plus water used, or an error of about one-half calory in the ordinary determination. If, for instance, 1 gram butyl alcohol should be burned instead of sugar, the change in the system would be equal to 0.4685 gram water—an error of 0.019 per cent.

This is a very small error, and, at the present, is perhaps altogether negligible.

The next question is, To what extent does this change of contents affect the heat evolved during the combustion?

This question refers to the same changes in the contents of the bomb as did the preceding one, but instead of studying their effect upon the water value of the bomb we want to see what the effect will be upon the determination of heat of combustion when the factor for the bomb and the water used remains the same.

In the case of the sugar there was an increase of 0.2603 gram water in the bomb, which, raised to 1.7° C., would equal about one-half calory held by it. The correction will, in other words, in the case of sugar, be the same whichever way we apply it, but this is not necessarily true of all substances burned. As said before, the correction is so small that it need seldom be considered.

CONCLUSION.

From what has been said, then, we learn that there are many possibilities for error in the work with the bomb calorimeter. Undoubtedly many investigators in the past have worked with impure oxygen and

never questioned its purity. In the light of our present experience it is questionable whether Stohmann himself, by the use of a heated copper tube, could have removed the last traces of combustible gases from his oxygen.

The disappearance of nitric acid formed and its relation to the ash has not been taken into consideration, and it is only within a couple of years that the thermometer lag has come to be applied in the calculations of the results.

These overlooked or at times unknown difficulties, which have been referred to throughout this paper, may be the cause of some of the disagreements of results as experienced by different investigators and referred to in the earlier part of this paper.

From what has been done and said I believe we also have learned that much work is yet needed in the different lines indicated before the method for determinations of heat of combustion by means of the bomb calorimeter can be called perfect.

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